PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 :		(11) International Publication Number:
B05D 3/06	A1	WO 90/02613
		(43) International Publication Date: 22 March 1990 (22.03.90)

(21) International Application Number: PCT/AU89/00373

(22) International Filing Date: 5 September 1989 (05.09.89)

(30) Priority data:
PJ 0242 5 September 1988 (05.09.88) AU
PJ 0980 17 October 1988 (17.10.88) AU

(71) Applicant *(for all designated States except US)*: JAMES HARDIE & COY. PTY. LIMITED [AU/AU]; 1 Grand Avenue, Camellia, NSW 2142 (AU).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : COOKE, Anthony, Michael [AU/AU]; 2 Norfolk Place, Carlingford, NSW 2118 (AU). MANNOT, Walter, Franciscus [AU/AU]; 8 Terrey Road, Deniston, NSW 2144 (AU).

(74) Agent: SHELSTON WATERS; 55 Clarence Street, Sydney, NSW 2000 (AU).

(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.

(54) Title: A METHOD OF FORMING A FILM FOR PAINT

(57) Abstract

A method of forming a film of a water containing paint on a temperature sensitive substrate. A film of paint is applied to the surface of the substrate and subsequently the surface is irradiated with microwave radiation to heat the film of paint without overheating the substrate. In a preferred form at least the surface of the substrate is dried to a moisture content of less than about 7 % prior to application of the paint film.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic			SN	Senegal
CG	Congo	KR	Republic of Korea	SU	Soviet Union
CH	Switzerland	LI	Liechtenstein	TD	Chad
CM	Cameroon	LK	Sri Lanka	TG	Togo
DE	Germany, Federal Republic of	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		

"A METHOD OF FORMING A FILM FOR PAINT"

TECHNICAL FIELD

This invention relates to a method of forming a film of paint on temperature sensitive substrates. More particularly the invention provides for the curing of paint systems which hitherto have required heating processes in which the temperature of the substrates to which the paint is applied would be unacceptably elevated. The invention has application to all paints containing water and has particular application to zinc silicate paint systems and emulsion paint systems.

BACKGROUND ART

Zinc silicate paints based on sodium silicate have been used for many years to produce durable decorative coatings on a variety of substrates. When used on compressed asbestos cement substrates these paints provide durable coatings able to withstand external exposure for thirty years or more without significant

change in appearance. Moreover, zinc silicate paint systems are quite inexpensive compared to other paint systems capable of giving similar performance.

However, it has been hitherto not being possible to apply zinc silicate paints to the cellulose reinforced cement sheets that have replaced asbestos cement. This is because the method of curing zinc silicate paints required the heating of the painted article to about 350°F for approximately 20 minutes. It has been found that cellulose reinforced cement products cannot withstand this heating.

Emulsion paints are commonly cured by air drying or by accelerated drying with radiant heat or hot air. These paints consist of an emulsion of resin particles, pigment particles, surface active agents and other components in water. The paints lose their water when drying and the resin and pigment particles come together to form a film. The properties of the cured paint film are influenced primarily by the molecular weight of the resins in the film and their chemistry. In general films of high molecular weight will be harder and stronger than those of low molecular weight. Each particular resin or paint system has a minimum film forming temperature (MFT) below which film formation will not take place. Film formation, or coalescence as it is known, may be assisted by the incorporation of high molecular weight solvents into the paint formation

which have the effect of reducing the MFT. This enables the film forming ability of the paint to be altered to suit the conditions under which the paint film is to be applied. Use of coalescent solvents is more usual for resins of high molecular weight however it can have the effect of reducing the hardness of the final film if the coalescent solvent remains in the film after curing. Slow loss of this solvent usually occurs over a period of time after the painted article has been exposed to the atmosphere and the paint film is said to have cured out. Painted products which have not been exposed to the atmosphere may retain the coalescent solvents for an extended period of time and the paint coatings may remain soft. In the case of stacks of flat painted sheets the coating may remain susceptible to damage due to the abrasion of the sheets one against the other.

If the paints have been dried in air where water is removed by natural evaporation and the film formed spontaneously such films must have an MFT less than the atmospheric temperature. To obtain a hard coating it is usually necessary to incorporate large amounts of coalescent solvent into such a coating. It is possible to obtain a similar result using a hard resin with a high MFT if the curing can be achieved at an elevated temperature. These resins can be fully cured at the elevated temperature and after cooling they are fully

hardened thus making the painted article serviceable immediately. As with zinc silicate paint systems however, the disadvantage of curing at an elevated temperature is that the entire article to be painted must be heated to the required curing temperature. This is often not possible due to the temperature sensitive nature of some substrates. Additionally, after curing of the paint cooling can be required which results in a substantial waste of energy.

DISCLOSURE OF THE INVENTION

It is an object of this invention to provide a method of forming a film of a water containing paint on a temperature sensitive substrate which will overcome, or at least ameliorate, one of the foregoing disadvantages.

Accordingly, this invention consists in a method of forming a film of a water containing paint on a temperature sensitive substrate comprising the steps of applying a film of paint to the surface of the substrate and subsequently irradiating the surface with microwave radiation to heat the film of paint without overheating of the substrate.

As used herein the term "temperature sensitive substrate" is intended to refer to substrates of the kind unable to withstand the stoving conditions normally associated with the curing of zinc silicate paint systems and emulsion paint systems, typically above

about 120°C. It is estimated that in the method according to this invention the bulk temperature of the substrate, that is the temperature of the substantial portion of the substrate, does not exceed about 120°C.

Preferably, the method further comprises the step of drying at least the surface of the substrate to a moisture content less than about 7% prior to the application of the paint film. This drying is preferably achieved by the application of microwave radiation. It is also preferred that the method comprises the further step of heating the surface of the substrate to a temperature of about 60°C prior to the application of the paint film. It is believed that there is an additional advantage associated with initial drying because when the paint contacts the surface a thin cured layer is initially formed on the surface of the substrate by the migration of moisture into the drier surface of the sheet material. It is further believed that this process may assist in preventing the subsequent bubbling of the paint during application of the microwave radiation.

It will be apparent that in the case of cellulose reinforced cement sheet the substrate has a moisture level of around 18% when it is manufactured. This can reduce to as much as 6-7% in equilibrium during storage depending upon the ambient conditions. The degree of drying required in the case of cellulose reinforced

cement sheets can thus vary.

It is preferred that the applied energy density during irradiation of the painted surface is from 2.5 to 6.6 J/mm^2.

The method of this invention has been found to provide for the rapid curing of both the zinc silicate paints and emulsion paint systems on temperature sensitive substrates that would be damaged by the stoving conditions normally required for curing. It is believed that this is achieved because the paint films typically contain considerably more water than the substrate and are therefore heated more efficiently by the microwave energy. It is also possible that the chemical reactions involved during curing are favourably affected by the microwave irradiation. It will be apparent that the method of this invention also has the advantage that the paint films can be cured very rapidly in an on-line apparatus incorporating a microwave generator that necessity having large expensive drying ovens.

BEST MODES FOR CARRY OUT THE INVENTION

The following examples serve, by way of example only, to further illustrate the invention.

Example 1

Zinc silicate paint of the formulation given in Table 1 was mixed and ground for 3 minutes in a Waring Blender until its fineness of grind was measured to 6 on

a Heguan gauge. The viscosity of the formulations was then adjusted to 0.4 poise and it was allowed to stand for 60 minutes.

TABLE 1: Gun Metal Zinc Silicate Paint

Zinc Oxide	100
Titanium Dioxide	40
Iron Oxide (Marigold Yellow)	0.3
Iron Oxide (Yellow)	2.0
Iron Oxide (Black)	0.34
Ground Silica	15
Sodium Silicate Solution	300
Water	150

The formulation was applied to compressed cellulose reinforced sheet preheated to 60°C. It was cured for 12 minutes in a microwave oven of 680W power input at 2450MHz fitted with a rotating table. Satisfactory performance with regard to appearance was achieved, however the boil resistance was barely satisfactory and the acid extraction result was not satisfactory.

Example 2

The formulation of Example 1 was modified with up to 10% by weight of a 10% solution of $ZnSO_4$ in water to the weight of sodium silicate solution. It was found that above 4% by weight of $ZnSO_4$ solution, the paint gelled prematurely. However, below this amount, the paint applied and cured as in Example 1 had a boil resistance which was adequate and an extraction resistance which was improved but not satisfactory.

Example 3

A formulation was prepared and cured as described

in Example 2 but catalysed by 5% cadmium sulphate as a 10% solution in water. Satisfactory boil resistance was achieved with a satisfactory extraction resistance.

Example 4

The formulation of Example 1 was prepared, applied and cured with the addition of an ion exchanging calcium bentonite. Extraction resistance was unaltered but boil resistance was significantly improved.

Example 6 Continuously Cured Paints

Fibre-cement sheets were predried to a surface moisture content of less than about 7% in a microwave oven having at a power level of 20 Kw at a frequency of 2450 MHz. The oven included a belt conveyor to transport the sheets through the microwave radiation. Zinc silicate paint of the formulation given in Table 1 was applied at an approximate dry film thickness of 40µm and the sheets were cured by exposing them to various levels of power in the same continuous microwave oven.

Table 1:Formulation

Zinc Oxide (white seal)	30
Zinc Oxide (submicron)	70
Titanium Dioxide	20
Black Iron Oxide	22
Sodium Silicate	300
Cadmium Sulphate (10% w/w)	15
Water	85

The resulting painted product was tested for adequacy of cure by means of alkali extraction, boil resistance and stack breakdown tests with the results given in Table 2.

Table 2:Results of Testing

Microwave Energy J/mm^2	Extraction Value-HCl ml .01N	Boil Mark Rating (1-4)	Stack Breakdown Rating (1-5)	Substrate Condition -
5.3	2.1	4	3	Satisfactory
9.7	1.5	4	2	"
11.6	1.6	4	2-3	"
18.8	1.7	1-2	1	Charred

Example 7 Variation of substrate

Samples of plain uncompressed, patterned uncompressed and compressed fibre cement sheet were coated with the same paint formulation as above. The sheets were then cured at various power levels as described in Example 6 and tested as before. The results outlined in Table 3 were obtained.

Example 8

Fibre cement sheets were surface dried to less than about 7% moisture in a continuous microwave oven using microwave energy of 2450 MHz frequency. A pigmented emulsion paint without coalescent solvents was applied to fibre cement sheet by air assisted spray at a dry film thickness of approximately 30µm. Sheets were separately cured in the same continuous microwave drying oven at the rates of 2.5, 3.3, 5.0 and 6.6 Jmm^2 of

Table 3: Results of Testing

Substrate Type	Microwave Energy J/mm^2	Extraction Value-HCl ml .01N	Boil Mark Rating (1-4)	Stack Breakdown Rating (1-5)	Substrate Condition -
Uncompressed Plain		7.7	4	1-2	Satisfactory
Uncompressed Patterned	5.0	5.5	4	2	Satisfactory
Compressed		33.4	4	3-4	Satisfactory
Uncompressed Plain		9.5	4	1-2	Satisfactory
Uncompressed Patterned	6.7	21.4	4	2	Satisfactory
Compressed		34.5	4	2	Satisfactory
Uncompressed Plain		4.7	4	1-2	Satisfactory
Uncompressed Patterned	10.0	5.2	3-4	2-3	Satisfactory
Compressed		15.9	4	2-3	Delaminated
Uncompressed Plain		4.3	2-4	1	Satisfactory
Uncompressed Patterned	13.3	3.3	2-4	1	Charred
Compressed		5.4	2-4	1	Charred

microwave enrgy. Control sheets were also coated with paint and either air dried or subjected to a radiant cure at 60°C for 10 minutes. The painted and cured sheets were then tested using standard paint testing methods to give the following results.

Curing Condition	Cross Hatch Adh'n %	Blocking Resistance	Boil Resistance	Paint Appearance
Radiant 10 min	98%	Blocked	Softened	Good
Air Cure	97%	Blocked	Softened	Good
MW 2.5 J/mm^2	93%	Blocked	Softened	Good
MW 3.3 J/mm^2	94%	Blocked	Softened	Good
MW 5.0 J/mm^2	98%	Blocked	Softened	Good
MW 6.6 J/mm^2	92%	Blocked	Softened	Good

The Cross-Hatch Adhesion refers to the result of an adhesion test where the paint is scribed with a grid of 25 squareseach with a side of 5mm, a piece of adhesive tape is applied over the scribed area and then removed. The amount of the paint remaining after the test is estimated and reported. It will be seen that there is apparently an optimum microwave curing energy input rate which will result in the greatest adhesion.

The blocking resistance refers to the ability of painted sheets to resist sticking to the backs of

adjoining sheets when stacked (and forming a solid block). No significant change in the blocking resistance was observed with this system with any particular curing regime. This however is more a reflection of the paint resin system rather than the curing system.

Boil resistance is determined by subjecting the painted article to boiling water for a specified time, allowing the article to cool and then observing any changes to the cooled paint film. In this case the microwave curing did not affect boil resistance compared to the air or radiant cured films.

CLAIMS

1. A method of forming a film of a water containing paint on a temperature sensitive substrate comprising the steps of applying a film of paint to the surface of the substrate and subsequently irradiating the surface with microwave radiation to heat the film of paint without overheating of the substrate.

2. A method as claimed in claim 1 further comprising the step of drying at least the surface of said substrate to a moisture content of less than about 7% prior to the application of said paint film.

3. A method as claimed in claim 2 wherein the drying is achieved by the application of microwave radiation.

4. A method as claimed in any one of claims 1 to 3 further comprising the step of heating the surface of said substrate to a temperature of about 60°C prior to the application of said paint film.

5. A method as claimed in any one of claims 1 to 4 wherein the bulk temperature of the substrate does not exceed about 120°C.

6. A method as claimed in any one of claims 1 to 5 wherein the applied energy density during said subsequent irradiating of the surface with microwave radiation is from 2.5 to 6.6 J/mm^2.

7. A method as claimed in any one of claims 1 to 6 wherein the frequency of the microwave radiation is about 2450 MHz.

8. A method as claimed in any one of claims 1 to 7 wherein said paint film thickness is about 40 µm.

9. A method as claimed in any one of claims 1 to 8 wherein said paint is cured by the evaporation of water.

10. A method as claimed in claim 9 wherein said paint is a zinc silicate paint system.

11. A method as claimed in claim 9 wherein said paint is an emulsion paint system.

12. A method as claimed in any one of claims 1 to 11 wherein said substrate is a fibre reinforced cement sheet.

13. A method as claimed in any one of claims 1 to 11 wherein said substrate is a compressed fibre reinforced cement sheet.

14. A method of forming a film of paint containing water on a temperature sensistive substrate substantially as herein described with reference to any one of Examples 1 to 8 herein.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 89/00373

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.[4] B05D 3/06

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
IPC	B05D 3/06

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8

AU: IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category*	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
X	US,A, 3506467 (ULRICH) 14 April 1970 (14.04.70) See column 1 lines 13-24.	1,7,9
X	GB,A, 2061130 (SCHENECTADY-MIDLAND LTD.) 13 May 1981 (13.05.81) See See claims 1-17 and page 4 lines 48-59.	1,7,9
X	FR,A, 2374968 (JEHL) 21 July 1978 (21.07.78) See claim 1 & 2 and Example 1.	1,7,9
A	FR,A, 2458323 (ANVAR) 2 January 1981 (02.01.81)	
A	WO,A, 87/00004 (BONE DIAGNOSTIC CENTER INC.) 15 January 1987 (15.01.87).	

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12 December 1989 (12.12.89)	18/12/89
International Searching Authority	Signature of Authorized Officer
Australian Patent Office	R.B. CAMPBELL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL APPLICATION NO. PCT/AU 89/00373

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Members		
GB 2061130	AU 60934/80	CA 1157805	DE 3036315
	FR 2466485	JP 56073574	ZA 8004842
	AU 60935/80	DE 3036314	FR 2466484
	IT 1141007	JP 56057829	ZA 8004839
	AU 61409/86		
WO 8700004	EP 229166	JP 1105159	US 4839194
	ZA 8604946		

END OF ANNEX